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SOLID PHASE DISPROPORTIONATION OF MERCURY COMPOUNDS

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R.G. Mikaelyan, A.P. Baranov, A.K. Mal'tsev, D.M. Nefedov

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SOLID PHASE DISPROPORTIONATION OF MERCURY COMPOUNDS

R.G. Mikaelyan, A.P. Baranov, A.K. Mal'tsev, D.M. Nefedov

Disproportionation of organomercury compounds in solution is well-known and has been fully studied [1]. We discovered that similar reactions take place quite readily in solid phase—when mercury compounds are compressed with potassium bromide (150 mg KBr with $\sim 1 \times 10^{-2}$ moles of each of the reactants, compressed at a pressure of ~ 2 T/cm^2).

The following pairs of substances were studied, taken in equimolar quantities: $(C_6H_5)_2Hg$ (I) + $HgCl_2$ (II), I + Cl_3CHgCl (III), I + $(Cl_3C)_2Hg$ (IV), II + $C_6H_5HgCCl_3$ (V). The solid solutions were kept at room temperature and periodic recordings of their infrared spectra were made in the range of 400-1700 cm^{-1}. We selected the necessary charateristic frequencies of the initial and anticipated compounds with reference to the data in [2].

An analysis of the spectra indicated that in all cases a corresponding disproportionation took place.

$$R_2Hg + R'HgR'' \rightarrow RHgR' + RHgR''$$

$$R = C_6H_5,\ Cl;\ R' \text{ and } R'' = Cl_3C,\ Cl,\ C_6H_5.$$

The reaction between (I) and (II) proceeded quite readily, terminating completely after one hour at 20° and resulting in the formation of C_6H_5HgCl (VI) (showing bands of 456, 725 and 1330 cm^{-1}). The interaction of (I) and (III) at $\sim 20°$ took place more slowly (about 60 percent conversion in 80 hours),

accompanied by the formation of [VI] and [V] [ν 452 cm^{-1}]. However, at 70° this reaction took place in about 4 hours. [I] reacted with [IV] even at a slower rate [~60 percent in 100 hours at ~20°], resulting in [V] and products of its partial hydrolysis—C_6H_5HgOH [ν 454, 515, 598, and 618 cm^{-1}] and $HCCl_3$ [ν 760 and 1218 cm^{-1}]. The observed reduction in the rate of reaction with the assistance of [I] during the conversion from [II] to [III] and [IV] agrees with the anticipated reduction of electrophilicity of the mercury atom in these compounds due to its intramolecular coordination with one of the chlorine atoms of the CCl_3 group [3].

The interaction of [II] and [V] resulted in [VI] and [III] [ν 715 and 770 cm^{-1}], with roughly 80 percent conversion in 10 hours at ~20°.

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